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The Management of Mercury in the Dental-Unit Wastewater Stream

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Introduction

The heavy-metal content of dental-unit wastewater has become an issue of increasing importance to the United States Navy Dental Corps, and regulations governing heavy-metal discharge into the environment are becoming more stringent. Mercury (Hg) remains among the top 20 hazardous substances listed on the Agency for Toxic Substances and Disease Registry/Environmental Protection Agency (EPA) priority list. A recent EPA conference on Mercury in the Midwest (1), held 22-23 October 1996, highlighted the need for keeping Hg out of medical waste and out of the wastewater stream. Heavy metals including Hg are present in Great Lakes water and fish (2), and the consumption of fish contaminated with heavy metals represents an important source of human exposure (2-4). The recently implemented Great Lakes Water Quality Guidance criteria (5) call for an ambient Hg water level of 1.3 ng/liter (parts per trillion, ppt) for the protection of wildlife. Such guidelines have become a force for lowering the permitted release of pollutants into public sewage treatment facilities.

In 1997 it was estimated that dental facilities in the United States used 40 metric tons of Hg (6). The Seattle Metro Study (7) and a later study by Barruci et al. (8) reported that about 12-14% of the Hg load to local sanitary districts originated from dental clinics. There have been few studies investigating the environmental aspects of the metals released from dental amalgam (9). Recent collaborative studies by Naleway et al. (10) and Cailas et al. (11) were the first to rigorously define

the dental amalgam-wastewater stream. A later study (12) demonstrated the presence of significant levels of soluble ($<0.45 \mu\text{m}$) Hg in the fluid portions of dental-unit wastewater (13).

Industrial wastewater-treatment technologies have been developed to address specific manufacturing applications (14). However the development and implementation of waste-treatment technologies for dental-operatory wastewater is in its infancy (15, 16). Developing effective, nontoxic, and cost-effective treatments has been difficult due to the relatively small quantity of dental-operatory wastewater generated and its heterogeneous nature (10, 11, 17, 18).

Regulatory Background

Reorganization Plan 3 established the United States EPA in 1970 (19). This Reorganization Plan transferred a variety of assets to the EPA including research, monitoring, standards, and enforcement activities. A motivating effort of the reorganization plan was to create a single integrated agency to oversee the abatement and control of pollution on a national level. The EPA is currently organized into a headquarters office in Washington DC and 10 regional offices. Regional Administrators head the Regional Offices and report directly to the Administrator for the execution of the Agency's program within their Regions. The President with the consent of the Senate appoints the EPA administrator.

Under Section 402 of the Clean Water Act, all point source discharges of pollutants to waters of the United States (lakes, rivers, wetlands, etc.) must be authorized under a National Pollutant Discharge

Elimination System (NPDES) permit. In addition to direct discharges to US waters, industrial discharges to sanitary sewer systems (indirect discharges) must also meet standards and other local limitations designed to protect the water treatment facilities of the publicly owned treatment works (POTWs). NPDES discharge permits are not required for these indirect discharges which fall under pollution control standards implemented through locally issued permits under the Industrial Pre-treatment Program.

Of major importance is the fact that most POTWs were not designed to treat toxic pollutants. As a result, dischargers, including dental treatment facilities, may be required to pretreat their effluent prior to discharge. This is precisely what transpired at the Naval Dental Center, Norfolk (12). Waste pre-treatment consists of techniques or “management practices” used to reduce or eliminate contaminants that interfere with the microorganisms used by local POTWs to facilitate waste treatment.

Local Limits

Local POTWs have the option to set local discharge limits at or below those adopted by the NPDES. A survey conducted by the Association of Municipal Sewerage Agencies (AMSA) taken at the 1998 AMSA/EPA Pretreatment Coordinator’s meeting showed the average local discharge limits for industrial discharge of Hg to be 0.0875 mg/liter (n=42, range=0.00002-to-2 mg/liter). Two agencies did not have local limits for Hg, one agency had a narrative pollution prevention standard for Hg, and one agency had a tiered Hg limit based on flow rates from facilities. This variability in local discharge limits can create difficulties for Navy dental treatment facilities trying to meet their POTW discharge limits. NDRI is currently assembling a database of national discharge limits that will be made available to dental treatment centers at a future date.

Analytical Methods

Historically, allowable Hg limits tend to be adjusted downwards as analytical methods became more sensitive. Until recently the method of choice for the analysis of Hg in water was EPA Standard Method 245.1 (20). This cold vapor atomic

absorption technique is based on the ultra-violet light absorption by mercury vapor (253.7 nm) to determine Hg levels. The typical detection limit for this method is 0.2 µg/liter (parts per billion, ppb). NPDES discharge limits for Hg are based upon the detection limit of this standard method. In May of 1999, the EPA Office of Water promulgated a new standard method for the analysis of Hg in wastewater. As published in the Federal Register (21), Method 1631, Revision B is for the determination of Hg in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry. The new method allows for the determination of Hg at 0.5 ppt, and has improved accuracy and precision at low Hg levels when compared to Method 245.1. In addition, it allows for Hg determinations at ambient water quality criteria levels for the first time. Method 1631 has four components: Sample preparation involves a chemical “cleaning” step (oxidation-reduction) to produce volatile elemental Hg in an aqueous solution. The Hg is purged from the aqueous solution onto a gold-coated sand trap. The trapped mercury is thermally desorbed from the gold trap into a flowing gas stream into the cell of a cold-vapor atomic fluorescence spectrometer.

The 400-fold decrease in the detection limit for Hg achieved with standard method 1631 will necessitate the lowering of Hg discharge limits by POTWs.

Treatment Technologies

NDRI’s studies were initiated as part of an effort to remove Hg from the wastewater of a large dental treatment facility in Virginia (12). Hg spikes, detected by the local POTW at a pumping station across the street from the dental facility, led to sampling of the air/water separating tanks of the dental facilities vacuum system. Hg levels of 20-to-10,000 mg/liter were measured in these tanks. These high Hg levels resulted in the clinic being disconnected from the local POTW waste lines. Clinic personnel began collecting the dental-unit wastewater in 55-gallon drums and incurred disposal costs of over \$900.00 per drum.

In an attempt to meet local POTW mandated discharge limits (0.1mg/liter average daily discharge and 0.05 mg/liter average monthly discharge) the clinic installed commercially available centrifugal

amalgam separators. Samples of the centrifuge-treated wastewater showed a mean total Hg concentration of 3.91 mg/liter (n=6, SD=0.274). Soluble Hg concentrations were found to be 0.37 mg/liter (n=6, SD=0.064). Therefore, mechanical separation was not sufficient to meet local POTW discharge limits and appeared to increase Hg levels when compared with sedimentation alone. Further analyses determined that the concentrations of soluble Hg in the centrifuge-treated samples were higher than local POTW discharge limits.

The centrifuges were removed and the first NDRI designed system employing a combination of sedimentation, filtration, and ion exchange technologies was installed. A standard air-water separation tank was modified to enhance sedimentation. The clarified wastewater was then pumped through a graded series of filters and finally through cation exchange columns prior to discharge into waste lines. This system reduced Hg levels sufficiently for the POTW to allow dental facility reconnection to the sewer system. The NDRI modified settling tank and method has been awarded a United States patent (22).

An additional important finding of this effort was that a large amount of Hg is retained in wastewater lines. Some portion of amalgam waste never leaves the building, but is deposited in the wastewater lines. Five copper waste lines serving the dental-unit wastewater stream were collected and analyzed for total Hg using Standard Method 7471. An average of 1097 mg Hg per kg of pipe was found, with a range of 606-to-1603 mg/kg (SD=399). This retained Hg can be solubilized through the action of oxidizing line cleaners (23) and may in itself cause excessive Hg releases. The choice of line cleaners becomes critically important once a Hg removal system is in place, since certain of these chemicals can cause release of Hg trapped in lines between pre-treatment equipment and the local POTW connection.

Commercially available polymers have provided an effective treatment option for some dental facilities. NDRI tested the ability of two such polymers, individually and in combination, to remove Hg from dental-operator wastewater (24). The two polymers selected for this study are designed to either coagulate or filter Hg containing

waste (Nalco polymers N8186 and N8702, Nalco Chemical Company, Naperville, IL). The first of these polymers acts as a precipitant in aqueous solution and the second contains metal chelating molecules bound to a polymer backbone (26,27).

The polymer based treatment system is currently on-line pre-treating the wastewater stream of a large 45-chair dental clinic at Naval Dental Center, Great Lakes, IL. A standard plate and frame filter press dewateres the sludge produced by the pre-treatment process. The dewatered sludge is sent for recycling at a licensed Hg retorting facility. Hg levels leaving the press have been as low as 9 µg/liter.

Two Hg binding materials are currently being tested as a possible technology to pre-treat dental-unit wastewater. The first, Keylex® resin (Solmetex, Inc., Billerica, MA) is being tested at a 35-chair dental-treatment facility at Great Lakes, IL. The wastewater is pumped from four 50-gallon air/water separating tanks into a 125-gallon pre-treatment tank where chlorine is added to disinfect and oxidize the waste. Gross filtration is used to remove large particles prior to its passing through 25µm and 1 µm filters. The filtered waste then flows through cartridges containing the Keylex® resin. The flow rate is maintained at <250 ml/minute. Baseline Hg levels from the holding tank averaged 6.3 mg/liter (n=10, SD=1.2). The Hg levels of the Keylex® treated samples were all at non-detectable levels when a method detection limit of 0.2 µg/liter was employed (28). Two earlier samples were found to have non-detectable levels of Hg using standard method 1631. Work continues on optimizing this system and determining the cartridge replacement intervals.

The second material being tested by NDRI is a microbial biosorbent derived from genetically engineered bacteria. These bacteria express a metal binding motif on their cell surface. This biosorbent is capable of removing at least 94% of Hg from dental wastewater in bench top jar testing (29). Other devices are being constructed and will soon be installed at test clinics for evaluation and modification. Some of these may be suitable for use at clinics with 30 or more chairs and others for clinics with four or fewer chairs.

Summary

The issue of heavy metal contamination of dental-unit wastewater is becoming a high profile critical issue for the Navy Dental Corps. The promulgation of Standard Method 1631 with a detection limit in the part per trillion range will certainly result in lower NPDES permitted discharge limits. The good news is that technology is currently available, and being developed, that allows for the achievement of Hg removal necessary for continuous dental clinic waste discharge into POTW controlled wastewater lines. These new pre-treatment devices can be installed and maintained for considerably less than the cost of collecting and disposing of dental wastewater at more than \$900.00 per 55-gallon drum.

NDRI is currently evaluating existing and emerging technologies for removal capability and cost effectiveness (for both installation and maintenance) as a function of clinic size. In some cases chair-based pre-treatment may be most efficient and in other cases clinic-based pre-treatment may be the preferred route.

An upcoming Scientific Update will focus on the issues of solid waste disposal including scrap amalgam and spent amalgam capsules. Solid waste issues fall under Resource Conservation Recovery Act (RCRA). This act gives the EPA authority to define and regulate hazardous waste.

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